Historic, archived document

Do not assume content reflects current scientific knowledge, policies, or practices.

Reserve
A381
R31

ARS 72-35
January 1965

LEVOPIMARIC ACID

A Product for Industry

U. S. DE[illegible]
NATIONAL A[illegible]CULTURAL LIBRARY
MAR 2[illegible]
CURRENT S[illegible] RECORDS

Agricultural Research Service
UNITED STATES DEPARTMENT OF AGRICULTURE

Trade names are used in this publication solely for the purpose of providing specific information. Mention of a trade name does not constitute a guarantee or warranty of the product by the U. S. Department of Agriculture or an endorsement over other products not mentioned.

PREFACE

The principal purpose of this publication is to apprise industry of opportunities for profitable new commercial ventures arising from research conducted by USDA's Agricultural Research Service on naval stores products. In addition, it provides a medium through which the Southern Utilization Research and Development Division can better serve the naval stores industry and, in return, receive practical guidance for future research designed to benefit agriculture, processors, and the consumer.

LEVOPIMARIC ACID

A Product for Industry

by
G. W. Hedrick, R. V. Lawrence, H. B. Summers, Jr.,
and L. W. Mazzeno, Jr.[1]

INTRODUCTION

The presence of moderately large quantities of levopimaric acid in pine oleoresin provides a source for an inexpensive, reactive, potentially useful chemical with an unusual complex structure. Based on recent USDA developments a process is now available for the isolation of levopimaric acid in good yields from crude pine gum without appreciable effect on the properties of the coproducts, namely turpentine and the residual rosin.

This achievement provides industry with an opportunity to increase profits from naval stores operations and to diversify outlets for pine gum products. This report affords a brief exposition of the process, the properties of the acid, its potential uses, and a preliminary cost estimate. Detailed information for the commercial production of levopimaric acid can be obtained from the USDA Naval Stores Laboratory in Olustee, Fla.

PROPERTIES

Name:	Levopimaric acid (2, 3, 4, 4b, 5, 9, 10, 10a-octahydro-7-isopropyl-1, 4a-dimethylphenanthrene-1-carboxylic acid)
Formula:	$C_{20}H_{30}O_2$
Appearance:	Colorless crystals
Molecular weight:	302. 24
Melting point:	151-152° C. $[\alpha]^{25}_{D}$ -278°
Neutral equivalent:	302. 24
Solvents:	Soluble in alcohol. ether benzene; less soluble in hexane

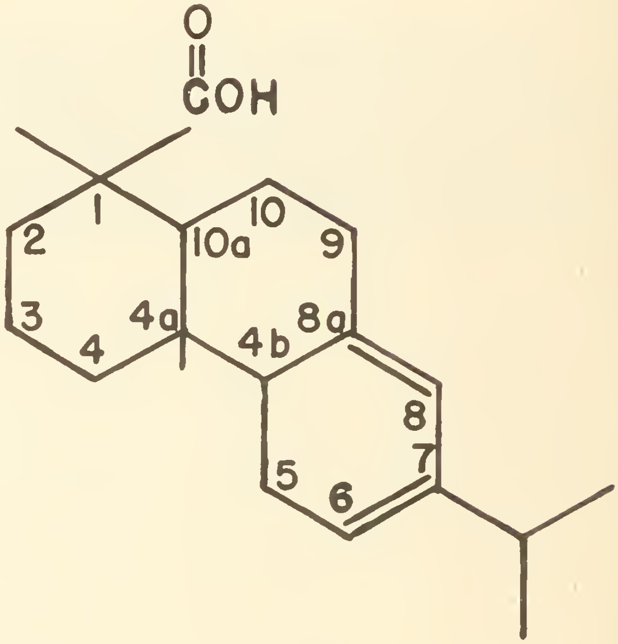

Figure 1. --Structure of levopimaric acid.

Levopimaric acid has been reported to disproportionate in ether solution on long standing. Alcoholic hydrogen chloride will convert the product to abietic acid in a few hours. Levopimaric acid isomerizes thermally, 150-200°, giving palustric, neoabietic, and abietic acids.

Reactions:	Selected reactions of levopimaric acid are listed in the diagram following.

---

[1] The authors express appreciation to Mr[illegible] M. B. S[illegible] for her dire[illegible] [illegible]laboration in the overall planning, composition and writing of this report

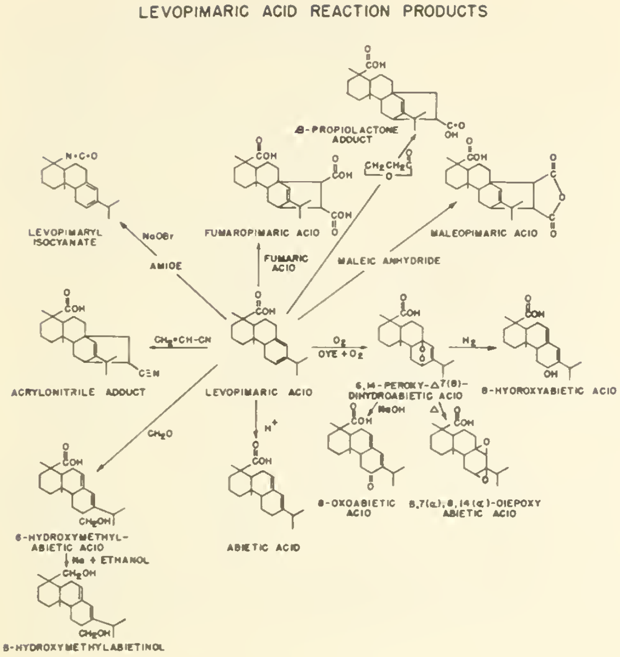

Figure 2. --Levopimaric acid reaction products.

POSSIBLE USES OF LEVOPIMARIC ACID

Adhesives:	Especially after conversion to maleopimaric acid followed by its reaction with urea and formaldehyde or with hydrazine and formaldehyde.
Agricultural:	Pesticides, fungicides, plant hormones; reaction products with acrylonitrile
Chemical:	Intermediate in synthesis of esters, amides, isocyanates, and in the synthesis of pharmaceuticals
Drugs:	Bactericidal formulations, suntan formulations and hydrazide as blood pressure depressant
Plastics--Synthetic Rubber:	Polymer modifiers--plasticizers, especially products formed by the reaction of the acid with betapropiolactone followed by esterification
Textiles:	Crosslinking agent with formaldehyde
Miscellaneous:	Printing Ink--esters or amides of levopimaric acid as in hair sprays or as paint additives.

ECONOMICS

Although the cost of producing levopimaric acid by this procedure has not yet been estimated in detail, some general information on manufacturing costs and capital investment can be deduced.

Since pine gum costs 8 cents a pound and since the recovered rosin and turpentine can be sold almost at market prices levopimaric acid of 95 percent purity can probably be manufactured for not over 40 cents a pound.

Since relatively simple and inexpensive equipment is required for the preparation of the acid, capital investment costs for the production of 1,000,000 pounds a year may not exceed $350,000.

TOXICITY

Toxic properties of levopimaric acid are not known. However, they should be similar to those of rosin which has been used widely for many years without adverse effects.

SAMPLES

Samples are available from the Naval Stores Laboratory, Olustee, Fla.

ACCOMPLISHMENTS

Levopimaric acid of high quality and in good yields has been isolated from pine gum. The formation of an amine salt by the reaction of oleoresin with 2-amino-2-methyl-1-propanol provides a means for the isolation of the desired acid. Specification grade turpentine and marketable grades of rosin were prepared from the filtrates after removal of the resin acid salts from the crude gum. The physical properties and the composition of the recovered rosin were shown to depend upon the amount of amine used in the precipitation of the resin acids. Ion-exchange resins, such as Amberlite IRC 50, were used successfully for the liberation of the free acid from the amine salt. A series of potentially useful derivatives were prepared from levopimaric acid.

PROCESS

Basically the process involves precipitating resin acid salts from pine oleoresin dissolved in acetone by the addition of an amine to the solution.

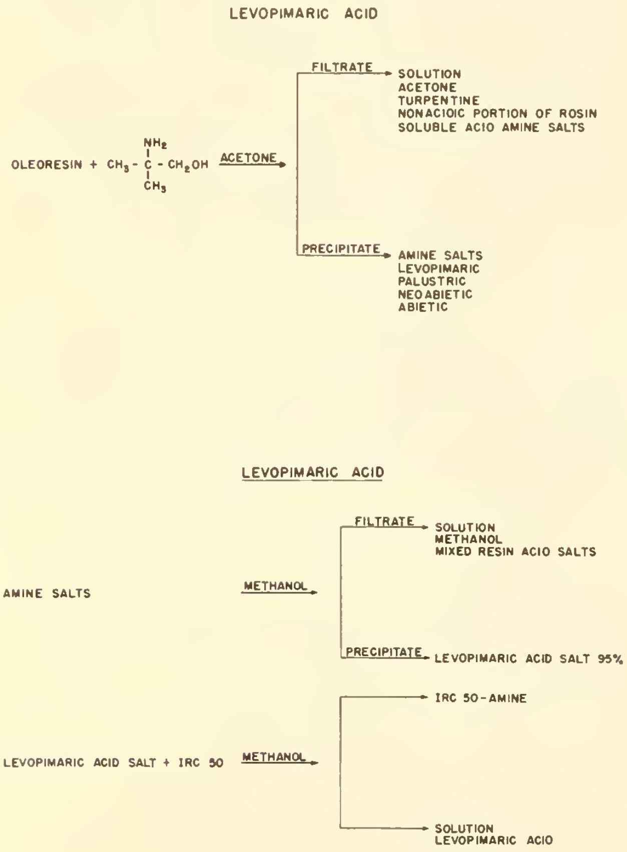

Figure 3A, 3B. --Levopimaric acid.

The procedure consisted of dissolving 3400 grams of pine oleoresin, containing approximately 25 percent levopimaric acid, in 13.44 liters of acetone followed by filtration to remove insolubles. Under reflux, 685 grams of 2-amino-2-methyl-1-propanol in an equal volume of acetone was added to the solution. The mixture was then stored at 5 to 10°C. for 15 hours. Filtration yielded a cake of resin acid salts, analyzing from 30 to 90 percent levopimaric acid salt, and an acetone solution of turpentine, the nonacidic portion of rosin, and minor amounts of the more soluble amine salts. Treatment of the cake with cold methanol removes the major portion of undesired resin acid salts. Recrystallization of the residue from methanol improves the purity to 95 percent. The pure levopimaric acid is obtained by passing a 4 percent methanol solution of the salt through an Amberlite IRC 50 column, followed by vacuum stripping of the solvent.

To recover the turpentine and rosin from the acetone filtrate, the solution is first passed over a bed of ion-exchange resins to rid the mixture of the amine. The individual components of the effluent are isolated by distillation.

Turpentine meeting specifications for a commercial grade is readily separated from the mixture. The residual rosin is sparged with steam at 165°C. to remove volatiles.

A suggested flow diagram is given in the charts that follow.

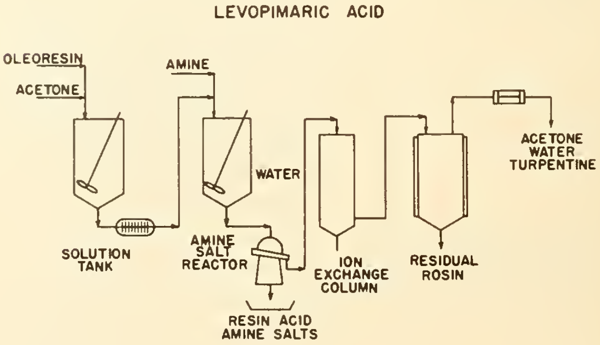

Figure 4A. --Levopimaric acid.

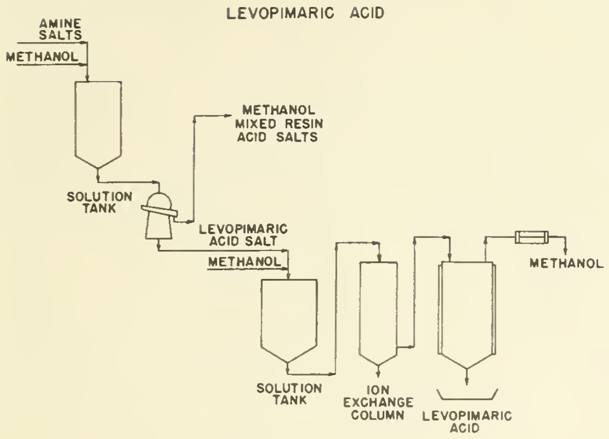

Figure 4B. --Levopimaric acid.

MATERIALS AND EQUIPMENT

Chemicals required
- Acetone
- Amberlite IRC 50
- 2-Amino-2-methyl-1-propanol
- Methanol
- Pine oleoresin

Equipment

Except for the ion-exchange column, standard mild carbon steel equipment is suitable for the production of high quality levopimaric acid from pine gum. Removal of the amine from the resin acid salts with dilute mineral acids requires use of a corrosion resistant material for the construction of the ion-exchange column. Explosion proof motors and electrical connections are of course required for safety.

SCOPE OF INVESTIGATIONS

A number of amines and other solvents have been examined for the isolation of the rosin acids. Acetone was found to be a good solvent and 2-amino-2-methyl-1-propanol was the most selective amine of the group tested for the isolation of levopimaric acid.

The effect of varying the amount of amine used to form the salts was studied. The composition of the resin acid salts produced ranged from 33 to 95 percent levopimaric acid. Procedures were developed for purifying salts varying widely in content of levopimaric acid.

Pine oleoresins from slash and longleaf varieties were used in the studies.

Solubility data for levopimaric acid in acetone and methanol were determined.

The properties of the residual rosins obtained following the removal of the resin acids were determined.

Several ion-exchange resins were evaluated for the quantitative recovery of the amine from the solutions.

KEY PERSONNEL INVOLVED ON PROJECT

Naval Stores Laboratory, Olustee, Fla.[2]

R. V. Lawrence
G. W. Hedrick
H. B. Summers, Jr.

PUBLICATIONS

THERMAL ISOMERIZATION OF LEVOPIMARIC ACID. Loeblich, V. M.; Baldwin, D. E.; O'Connor, R. T.; and Lawrence, R. V. J. Am. Chem. Soc., 77(23): 6311-6313, 1955. (Reprint No. 1218

ACID ISOMERIZATION OF LEVOPIMARIC ACID. Baldwin, D. E.; Loeblich, V. M.; and Lawrence, R. V. J. Am. Chem. Soc., 78(9): 2015-2017, 1956. (Reprint No. 1297)

AIR OXIDATION OF RESIN ACIDS. I. PHOTOSENSITIZED OXIDATION OF LEVOPIMARIC ACID. Moore, R. N.; and Lawrence, R. V. J. Am. Chem. Soc., 80(6): 1438-1440, 1958. (Reprint No. 1606)

---

[2] One of the laboratories of the Southern Utilization Research and Development Division, Agricultural Research Service, U. S. Department of Agriculture.

A PREPARATION AND SOME OF THE PROPERTIES OF TRANS-6, 12-DIHYDROLEVOPIMARIC ACID-6, 14-ENDO-ALPHA-BETA-SUCCINIC ACID. Halbrook, N. J.; and Lawrence, R. V. J. Am. Chem. Soc., 80(2): 366, 1958. (Reprint No. 1611)

PREPARATION OF 6-HYDROXYDEHYDROABIETIC ACID FROM THE PHOTOPEROXIDE OF LEVOPIMARIC ACID. Moore, R. N.; and Lawrence, R. V. J. Am. Chem. Soc., 81(2): 458-460, 1959. (Reprint No. 1760)

AIR OXIDATION OF RESIN ACIDS. II. THE STRUCTURE OF PALUSTRIC ACID AND ITS PHOTOSENSITIZED OXIDATION. Schuller, W. H.; Moore, R. N.; and Lawrence, R. V. J. Am. Chem. Soc., 82(7): 1734-1738, 1960. (Reprint No. 1932)

PHOTOSENSITIZED OXIDATION OF A TRANS DIENE AND THE CONFIGURATIONS OF THE PINE GUM RESIN ACIDS. Schuller, W. H.; and Lawrence, R. V. Chem. & Ind., 4, 105-106, 1961. (Reprint No. 2073)

THE DIELS-ALDER REACTION OF LEVOPIMARIC ACID AND ITS USE IN QUANTITATIVE DETERMINATIONS. Lloyd, W. D.; and Hedrick, G. W. J. Org. Chem., 26, 2029-2032, 1961. (Reprint No. 2137)

AIR OXIDATION OF RESIN ACIDS. III. THE PHOTOSENSITIZED OXIDATION OF NEOABIETIC ACID AND THE CONFIGURATIONS OF THE PINE GUM RESIN ACIDS. Schuller, W. H.; and Lawrence, R. V. J. Am. Chem. Soc., 83, 2563-2570, 1961. (Reprint No. 2142)

A PREPARATION AND SOME OF THE REACTIONS OF THE DIELS-ALDER ADDUCTS OF LEVOPIMARIC ACID AND ACRYLONITRILE. Halbrook, N. J.; Wells, J. A.; and Lawrence, R. V. J. Org. Chem. 26, 2641, 1961. (Reprint No. 2185)

THE ULTRAVIOLET IRRADIATION OF THE CYCLOHEXA-1, 3-DIENE, LEVOPIMARIC ACID. Schuller, W. H.; Moore, R. N.; Hawkins, J. E.; and Lawrence, R. V. J. Org. Chem. 27, 1178, 1962. (Reprint No. 2319)

LEVOPIMARAMIDE AND THE HOFMANN REACTION. Lloyd, W. D.; and Hedrick, G. W. J. Org. Chem., 28(4): 1156-1157, 1963. (Reprint No. 2525)

ISOLATION OF RESIN ACID MIXTURES RICH IN LEVOPIMARIC ACID FROM PINE GUM. Summers, H. B., Jr.; Lloyd, W. D.; and Hedrick, G. W. Ind. & Eng. Chem., Prod. Res. & Dev., 2(3): 173-177, 1963. (Reprint No. 2595)

GUM ROSIN MODIFIED WITH BETA-PROPIOLACTONE IN UNSATURATED POLYESTERS. Halbrook, N. J.; Lawrence, R. V.; Dalluge, M. D.; and Stein, G. A. Ind. & Eng. Chem., Prod. Res. & Dev., 2(3): 182-185, 1963. (Reprint No. 2597)

STRUCTURE AND STEREOCHEMISTRY OF DIELS-ALDER ADDUCTS OF LEVOPIMARIC ACID. Halbrook, N. J.; Lawrence, R. V.; Dressler, R. L.; Blackstone, R. C.; and Herz, W. J. Org. Chem. 29, 1017, 1964. (Reprint No. 2726)

PHOTOSENSITIZED OXIDATION OF PINE GUM TO YIELD PEROXIDES. Schuller, W. H.; Minor, J. C.; and Lawrence, R. V. Ind. & Eng. Chem., Prod. Res. & Dev., 3, 97-100, 1964. (Reprint No. 2732)

DIOLS FROM RESIN ACID MIXTURES. Parkin, B. A., Jr.; Settine, R. L.; and Hedrick, G. W. Ind. & Eng. Chem., Prod. Res. & Dev. (In press)

REACTION OF LEVOPIMARIC ACID WITH FORMALDEHYDE. Parkin, B. A., Jr.; and Hedrick, G. W. J. Org. Chem. (In press)

ISOLATION OF RESIN ACID MIXTURES RICH IN LEVOPIMARIC ACID FROM PINE GUM. ANALYSIS BY GAS-LIQUID CHROMATOGRAPHY AND MATERIALS COST ESTIMATES. Summers, H. B., Jr.; Parkin, B. A., Jr.; Joye, N. M., Jr.; and Hedrick, G. W. Ind. & Eng. Chem., Prod., Res. & Dev. (In press)